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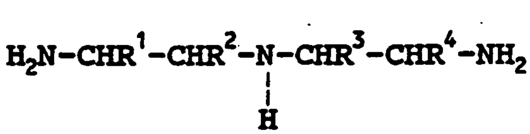

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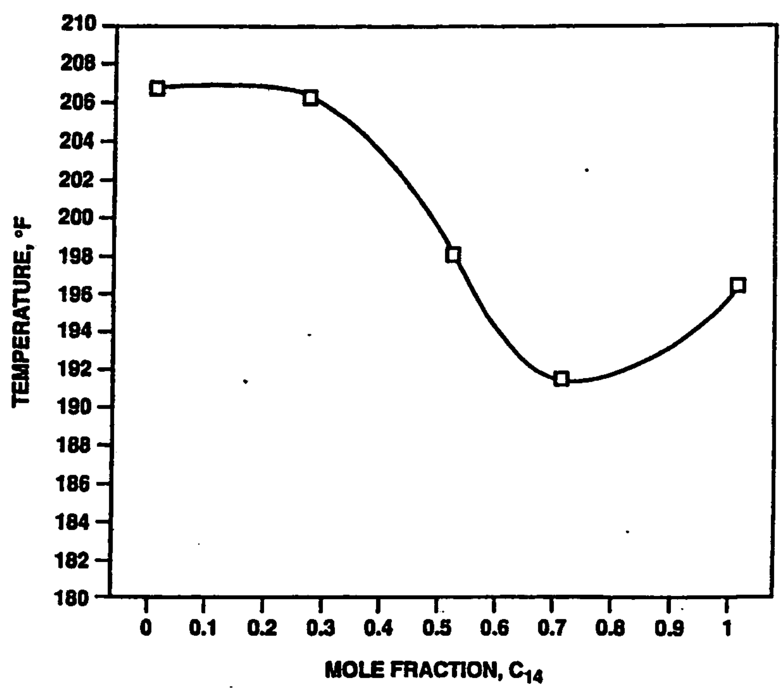

(57) Abstract

Disclosed are polyalkylenepolyamine compositions, comprising a di(C-alkyl)-diethylenetriamine of general structure (A), where either R^1 of R^2 is hydrogen and either R^3 or R^4 is hydrogen, and where the remaining two non-hydrogen R groups are independently either: (i) a long chain alkyl group having between 18 to 22 carbon atoms; or (ii) a sh rt chain alkyl group having 8 to 16 carbon atoms; provided that if both alkyl groups on the di(C-alkyl)-diethylenetriamine are long chain (i), r both alkyl groups are short chain (ii), then the compositi n contains a mixture of said structures some of which have l ng chain alkyl groups and some of which have short chain alkyl groups. A method of minimizing trialkanolamine formation in polyalkylenepolyamine compositions is also disclosed.

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LOW MELTING POLYALKYLENEPOLYAMINE CORROSION INHIBITORS

BACKGROUND OF THE INVENTION

This invention relates to novel hydrocarbon-soluble compositions which are useful in inhibiting corrosion and to a method of preventing corrosion using these compositions. The compositions have desirable low meltpoints.

Corrosion inhibition has been the subject of considerable interest over many years. The annual cost of replacing corroded metal components is staggeringly high.

In industrial cleaning operations, where aqueous solutions of acid serve to remove scale and other deposits from metallic surfaces of industrial equipment, inhibitors are used to reduce acid attack on the metals of construction during cleaning operations. In processing operations where some acid is present or may be generated, inhibitors are introduced to reduce the corrosiveness of the acid. In oil well operations, corrosion inhibitors are introduced during various stages and during secondary recovery operations. In all these operations, the corrosion inhibitor is generally in a form which is oil-soluble and dispersible, preferably miscible, in the liquid medium of the particular system.

Since the industrial equipment being protected by the inhibitor is often of considerable value or is often difficult and expensive to replace, significant importance has been given to the development of new and improved corrosion inhibitors. A wide variety of structures ar currently available in the marketplace.

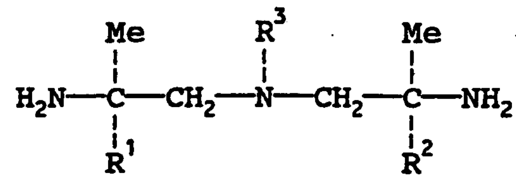
For example, corrosion inhibitors comprised of N-alkylamines or polyamines, having alkyl groups in the detergent range, are well known. See, for example, U.S. Patent No. 2,736,658 to Pfohl et al., which discloses aliphatic diamines of the structure:

$$\begin{array}{l} \mathrm{R} \\ | \\ \mathrm{HN(CH_2)_xNH_2} \end{array}$$

wherein R represents an aliphatic or alicyclic carbon chain attached to nitrogen of from 8 to 22 carbon atoms and x is a number from 2 to 10. Preferably, x is 3. These compounds are described as corrosion inhibitors, the effectiveness increasing greatly when the diamines are employed in the form of their fatty or rosin acid salts.

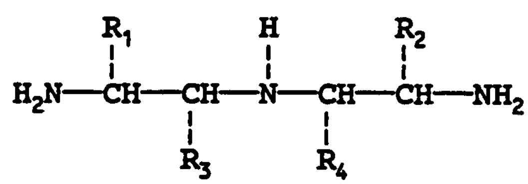
C-Alkyl diamines are known structures. For example, Kempter and Moser in J. Prakt. Chem. 34(14), 10411 (1966), CA 66:28324v describe the preparation of even-numbered 1,2- diamines from chromatographically pure even-numbered fatty acids. This procedure involves preparing the 2-bromoacid, reacting it with thionyl chloride and then ammonia to produce the 2-bromoamide, reacting the amide with 40-80 equivalents of aqueous ammonia to produce the 2-amino-amide and then reducing this product with lithium aluminum hydride. Aliphatic 1,2-diamines up to C_{18} are disclosed.

C-Alkyl polyamines having alkyl groups attached to carbon are also known structures. For example, U.S. Patent No. 4,293,682 to Kluger et al. discloses triamines are of the general formula:



where R^1 and R^2 can be lower alkyl of 1 to 5 carbon atoms and R^3 can be hydrogen. These triamines are useful as epoxy curing agents for polyepoxides

Recently, C-alkyl polyamines have been found to be useful corrosion inhibitors. In particular, U.S. Pat. No. 4,900,458 to Schroeder et al. discloses a polyalkylenepolyamine composition comprising a mixture of components including di(C-alkyl)-diethylenetriamine of the general formula:



where two of the four R groups are hydrogen, and the other two are alkyl groups independently containing from 10 to 28 carbon atoms. These polyalkylenepolyamine compositions of Schroeder et al., having the alkyl groups attached to carbon rather than nitrogen, exhibit improved corrosion inhibiting characteristics over commercial corrosion inhibitors.

The Schroeder patent (Column 6, lines 22-26) discloses:

> "Polyalkylenepolyamines having a mixture of alkyl groups containing more than one carbon chain length are especially preferred, as they have increased solubility, lower melting points and lower p ur points".

In particular, this patent discloses that mixtures of alkyl groups having between 18 and 22 carbon atoms are preferred. Indeed, all 27 examples in U.S. Patent No. 4,900,458 produce polyalkylenepolyamines with alkyl groups having 18 to 22 carbon atoms.

Unfortunately for some applications, the Schroeder et al. compositions are solids, having high meltpoints. They are therefore somewhat difficult to handle, process and formulate. Existing equipment, which is generally used to heat solid materials for handling in a wide variety of operations, often depend on low-pressure steam to provide heat input. For example, oil field service companies have blending facilities which utilize low pressure steam to blend components prior to shipment to the oil field. Schroeder's C-alkyl polyalkylenepolyamine compositions have meltpoints that abut or exceed the ability of this low-pressure steam heating equipment to readily or completely melt these solids. This makes their use difficult or impossible in these situations. Moreover, the long heating times needed to totally melt these solids are undesirable.

It is an object of this invention to provide polyalkylenepolyamine compositions which melt at temperatures below about 195°F, so that low-pressure steam heating equipment can be used to melt the composition. This will enable customers to readily process, handle and formulate these compositions using their existing equipment.

I have now discovered that C-alkyl polyalkylenepolyamine compositions comprising di(C-alkyl)-diethylenetriames have surprisingly low meltpoints when the c mposition comprises <u>both</u> long chain alkyl group containing between 18 to 22 carbon atoms, and short chain alkyl gr ups containing between 8 to 16 carbon at ms.

SUMMARY OF THE INVENTION

The pr sent inv ntion provides a hydrocarbon-soluble, corrosion inhibiting polyalkylenepolyamine composition comprising: a di(C-alkyl)-diethylenetriamine of the general structure

$$H_2N-CHR^1-CHR^2-\underset{\substack{|\\ H}}{N}-CHR^3-CHR^4-NH_2$$

where either R^1 or R^2, is hydrogen and either R^3 or R^4 is hydrogen, and where the remaining two non-hydrogen R groups are independently either (i) a long chain alkyl group having between 18 to 22 carbon atoms, or (ii) a short chain alkyl group having between 8 to 16 carbon atoms, provided that if both alkyl groups on the di(C-alkyl)-diethylenetriamine are long chain, (i), or both alkyl groups are short chain, (ii), then the composition contains a mixture of di(C-alkyl)diethylene-triamines, some of which have long chain alkyl groups and some of which have short chain alkyl groups. Preferred compositions of this invention have meltpoints below about 195°F.

The present invention further provides a method of inhibiting corrosion of a corrodible metal material which comprises contacting the metal material with an effective amount of the corrosion inhibitor composition of the invention.

The present invention is also concerned with a method of inhibiting corrosion of a corrodible metal material in or around a well through which a corrosive fluid is produced, which comprises contacting the metal material with an effective amount of the corrosion inhibitor composition of the invention.

In one embodiment, the present invention is a method of minimizing trialkanolamine formation in polyalkylenepolyamine compositions having the general structure:

$$H_2N\text{-}CHR^1\text{-}CHR^2\text{-}\underset{\mathrm{H}}{\underset{|}{N}}\text{-}CHR^3\text{-}CHR^4\text{-}NH_2$$

where R^1, R^2, R^3 and R^4 are independently hydrogen or an alkyl group having at least 8 carbon atoms comprising, reacting a mixture of alpha-olefin epoxides with ammonia in a reactor wherein 65 to 80% of the reactor volume is liquid, based on calculated liquid volumes at 60°F.

Among other factors, the present invention is based on my discovery that, for polyalkylenepolyamines corrosion inhibitors comprising di(C-alkyl)-diethyelenetriames which contain a mixture of long chain alkyl groups comprising chain lengths of 18 and 20 carbon atoms and already comprising many different chemical compounds, the meltpoint can be significantly reduced by including short chain alkyl groups of between 8 and 16 carbon atoms on these diethylenetriamines.

Additionally, the present invention is based on my discovery that, when preparing the polyalkylenepolyamines of this invention from epoxides and ammonia, there is synergy between the reactor fill volume and the ammonia to epoxide ratio. I have discovered that these two factors can be controlled to minimize the formation of undesirable, high- melting trialkanolamines.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of the meltpoints of various blends of C_{20-24} and C_{14} polyalkylenepolyamines.

Figure 2 is a trace from a DSC instrum nt showing the sec nd DSC endpoint for a polyalkylenepolyamine composition of this invention.

Figure 3 is an 'H nuclear magnetic resonance spectrum between 2.0 and 4.2 ppm.

DETAILED DESCRIPTION OF THE INVENTION

The Polyalkylenepolyamines

As used herein the term "long chain alkyl group" (LCAG) denotes an alkyl group having between 18 and 22 carbon atoms. Preferably, the LCAG is a mixture of alkyl groups, and more preferably the mixture contains at least 20 mole percent each of alkyl chains having 18 and 20 carbon atoms.

As used herein the term "short chain alkyl group" (SCAG) denotes an alkyl group having between 8 and 16 carbon atoms, or a mixture of alkyl groups having between 8 and 16 carbon atoms. Preferably, the SCAG is primarily a single carbon number. Preferred carbon numbers for the SCAG include 10, 12 and 14, more preferably 12 and 14.

As used herein, the term "C-alkyl" refers to an alkyl group directly bonded to carbon, and the term "di(C-alkyl)" refers to two alkyl groups directly bonded to two different carbon atoms. This usage of "C-alkyl" is similar to the expression "N-alkyl", which is well known in the art and means an alkyl group directly bonded to nitrogen.

As used herein, the term "unbalanced" or "unsymmetrical" refers to compounds of Structure 2 or 3 (below)

comprising both a LCAG and a SCAG on said structure. "Unbalanced" compounds, compositions and structures have at least two alkyl groups, one of which is a LCAG, the other of which is a SCAG.

In a preferred embodiment, the polyalkylenepolyamine composition of this invention comprises a mixture of structures which includes:

(a) at least two C-alkylethylenediamines and

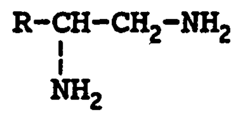
(b) at least two di(C-alkyl)-diethylenetriamines or di(C-alkyl)-piperazines, or a mixture thereof;

wherein the alkyl groups are unsymmetrical, containing both (i) long chain alkyl groups (LCAG) of between 18 and 22 carbon atoms and (ii) short chain alkyl groups (SCAG) of between 8 and 16 carbon atoms.

Generally, the composition of this invention will contain greater than 10% short chain alkyl groups, and preferably greater than 20%, based on the total number of C-alkyl groups. The ratio of (i) to (ii) will preferably range from about 0.2:1 to about 3:1, more preferably from 0.3:1 to 2:1.

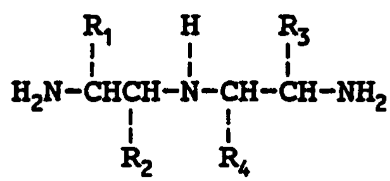
In a preferred embodiment, the composition contains unbalanced C-alkyl groups (i.e., both long and short chain alkyl groups) on the di(C-alkyl)-diethylenetriamine and the di(C-alkyl)-piperazine. Preferably, the SCAG contains either 12 or 14 carbon atoms.

Preferred polyalkylenepolyamine compositions of this inv ntion are a mixture of many compounds. This mixture generally includes at least two C-alkyl thylenediamin s of Structure 1 below. The R group in this composition comprises at least one LCAG and at least one SCAG.



(1)

The composition of this invention includes at least two di(C-alkyl)-diethylenetriamines or di(C-alkyl)-piperazines, or a mixture thereof. At least two di(C-alkyl)-diethylenetriamine of Structure 2 are present.

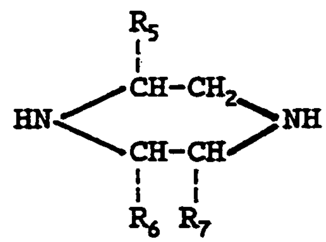


(2)

In Structure 2, R_1, R_2, R_3 and R_4 individually may be hydrogen or alkyl, provided that two of the R_1, R_2, R_3 and R_4 groups are hydrogen and two of the R_1, R_2, R_3 and R_4 groups are alkyl. Moreover, it is required that the composition contain both LCAG's and SCAG's, either on one molecule or on separate molecules having Structure 2. Preferably, either R_1 or R_2 is hydrogen and either R_3 or R_4 is hydrogen.

The compounds of Structure 2 can also be described as di(C-alkyl)-2,2'-diamino-diethylamines.

A cyclized di(C-alkyl) component may also be present, in addition to the di(C-alkyl)-diethylenetriamines. Generally, one or both of the di(C-alkyl)-piperazines of Structure 3 is present:



(3)

In Structure 3, one of the R_6 and R_7 groups is hydrogen and two of the other of the R_5, R_6 and R_7 groups are alkyl. The composition contains both LCAG's and SCAG's, either on the same molecule or on separate molecules of Structure 3. These di(C-alkyl)-diethylenepiperazines generally include compounds substituted at the 2 and 5 position, at the 2 and 6 positions, and at the 3 and 5 positions. These compounds may be described as 2,5- 2,6- and 3,5-dialkylpiperazines. It is believed that the above-described dialkyl compounds of Structures 2 and 3 are especially advantageous in controlling corrosion.

It is preferred that the di(C-alkyl)-diethylenetriamine comprise between 5 and 60 mole percent of the total composition, preferably between 5 and 45 mole percent and more preferably between 10 and 40 mole percent. In a preferred embodiment, the alkyl groups on Structure 2 are unbalanced. In this case, the unbalanced di(C-alkyl)-diethylenetriamine comprises between 2.5 and 30 mole percent of the total composition, preferably between 2.5 and 23 mole percent and more preferably between 5 and 20 mole percent.

Preferred alkyl groups are derived from the corresponding linear alpha-olefins. Even-numbered alpha-olefins are preferred.

Particularly preferred polyalkylen polyamin s are mixtures comprising Structure 1 with Structure 2 and/or

3, where the long chain alkyl group comprises between 25 to 75% of the alkyl groups, the remainder being short chain alkyl groups. Thes compositions have desirably lower meltpoints than compositions having only LCAG's.

As used herein, the term "polyalkylenepolyamine" refers to a mixture of compounds including the alkyldiamine of Structure 1, the higher dialkylpolyamines of Structures 2 and 3, and sometimes higher polyalkylenepolyamine oligomers. The alkyl chain can be linear or branched.

Although Structures 1, 2 and 3 above show primary and secondary amine groups, these amine groups can be substituted with one or more alkyl or amino-alkyl groups. These compounds are also encompassed by the term "polyalkylenepolyamine". As referred to herein, the term "polyamine" and "polyalkylpolyamine" are also used to mean "polyalkylenepolyamine".

These polyalkylenepolyamines can be present as either the free base or as a salt thereof, such as an organic or inorganic acid salt. Thus, the term "polyalkylenepolyamine" is also meant to include the free base, the ammonium salt form, or mixtures of the two.

<u>Preparation of Polyalkylenepolyamine</u>

The corrosion inhibiting composition of this invention can be prepared by a variety of methods.

One method, which produces unbalanced polyalkylene-polyamines, comprises:

a) preparing a mixture of functionalized alpha-olefins having between 10 to 24 carbon atoms and

having both long chain alkyl groups (i) and short chain alkyl groups (ii); and

b) reacting said functionalized alpha-olefin mixture with ammonia and optionally an amination catalyst to form a polyalkylenepolyamine composition comprising an unbalanced di(C-alkyl)-diethylenetriamine structure.

The alkyl groups referred to above exclude the 2 carbon atoms of the starting alpha-olefin. For example, a C_{22} alpha-olefin is converted to an epoxide having a long chain alkyl group of 20 carbon atoms.

Suitable methods of preparing unbalanced polyalkylene-polyamine composition include, but are not limited to the following: reaction of a suitable mixture of 1,2-dihaloalkanes with ammonia, in which the halogen may be chlorine, bromine or iodine; reaction of a suitable mixture of 1-epoxyalkanes with ammonia in the presence of a suitable catalyst, such as Raney nickel; reaction of a suitable mixture of 1-amino-2-alkanols or 2-amino-1-alkanols or mixtures thereof with ammonia in the presence of a suitable catalyst, such as Raney nickel; reaction of a suitable mixture of 1,2-alkanediols with ammonia in the presence of a suitable catalyst, such as Raney nickel; reaction of a suitable mixture of C-alkylaziridines with ammonia.

In the above-described methods, the functionalized alpha-olefins is a 1,2-dihaloalkane, a 1-epoxyalkane, an amino-alcohol, a 1,2-alkanediol, and an aziridine, respectively.

The mixture of functionalized alpha-olefins can be prepared in a number of ways. One method comprises converting an alpha-olefin mixture containing alpha-olefins having between 10 t 24 carbon atoms and having both long chain alkyl groups (i) and short chain alkyl groups (ii) into a mixture of functionalized alpha-olefins. Alternatively, a mixture of functionalized alpha-olefins can be prepared by blending functionalized alpha-olefins having LCAG's and SCAG's, for example blending epoxides prior to amination. The blending of functionalized alpha-olefins followed by amination is a preferred method of making unbalanced polyalkylenepolyamines. Suitable mixtures of reactants for preparing the unbalanced composition of this invention are those having both LCAG's and SCAG's. For example, a mixture of C_{20}, C_{22} and C_{14} epoxides.

A critical factor in determining what constitutes a suitable method for preparing the present composition is that the process must provide for the formation of the above-described di(C-alkyl) components, that is, components of Structure 2 and that both LCAG's and SCAG's are present in the polyalkylenepolyamines product.

In another embodiment, the polyalkylenepolyamine composition of this invention can be prepared by blending polyalkylenepolyamine compositions containing LCAG's with polyalkylenepolyamine compositions containing SCAG's. In this case, at least two polyalkylenepolyamines are prepared separately and then blended. The ratio of long chain to short chain groups can be adjusted, as required. Thus, one method of making the polyalkylenepolyamine composition of the invention comprises the steps of:

a) preparing a first polyalkylenepolyamine composition comprising a di(C-alkyl)-diethylenetriamine where both C-alkyl groups are long chain alkyl groups, containing between 18 to 22 carbon atoms; and

b) preparing a second polyalkylenepolyamine composition comprising a di(C-alkyl)-diethylenetriamine where both C-alkyl groups are short chain alkyl groups, containing between 8 to 16 carbon atoms; and

c) blending said first and said second compositions.

Polyalkylenepolyamine compositions prepared by blending do not result, however, in as great a meltpoint reduction as do compositions containing unbalanced polyalkylenepolyamine.

Preparation from 1-Epoxyalkanes

A preferred method of preparing the poly-alkylenepolyamines of the invention is by reaction of a suitable mixture of 1-epoxyalkanes with ammonia in the presence of a suitable amination catalyst, such as Raney nickel. In general, the 1-epoxyalkane mixture will contain from 10 to 24 carbon atoms. Epoxides containing 20-24 carbon atoms, preferably a mixture of C_{20}, C_{22} and C_{24} epoxides, will produce polyalkylenepolyamines with LCAG's. Epoxides containing 10-18 carbon atoms will produce polyalkylenepolyamines with SCAG's. The 1-epoxyalkane employed for the SCAG is preferably a single carbon number, while the 1-epoxyalkane employed for the LCAG is preferably a mixture of several carbon

numbers. The 1-epoxyalkanes may be branched or linear. Particularly useful 1-epoxyalkanes are derived from epoxidation of alpha-olefins obtained from the ethylene growth reaction.

The polyalkylenepolyamine composition of the invention can be prepared using procedures similar to those described in U.S. Patent No. 4,900,458, to Schroeder et al., which is incorporated herein by reference in its entirety. Additionally, sample preparations are found in the Examples.

While not wishing to be bound by theory, it is important to note that polyalkylenepolyamines prepared from a single carbon number 1-epoxyalkane, ammonia and a Raney nickel amination catalyst include a wide variety of compounds. Initial ring opening of the epoxide with ammonia produces two possible amino-alcohols. It is believed that the primary product is the 1-amino-2-ol. Both amino-alcohols yield one diamine when further reacted with ammonia in the presence of the amination catalyst.

Alternatively, the basic amine of the amino-alcohols can react with a second mole of epoxide to produce three isomeric dihydroxyamine dimers. Amination of these dimers yields the di(C-alkyl)-diethyelenetriamines. Under the reaction conditions, these dimers can also undergo ring closure to piperazines. Similarly trimers and tetramers can also be produced, depending on the ratio of ammonia to epoxide. Moreover, amination of the various amino-alcohols and polyhydroxyamines is generally not complete. Thus, a single carbon number 1-epoxyalkane yields a polyalkylenepolyamine composition containing a wide variety of compounds. These includ :

A. one C-alkylethylenediamine;

B. three di(C-alkyl)-diethylenetriamines (various positional isomers);

C. two di(C-alkyl)-piperazines (positional isomers);

D. two amino-alcohols, which are formed by incomplete amination, the 1-amino-2-ol predominates;

E. a variety of tri(C-alkyl)-triethylenetetra-amines;

F. a triamine species of Structure 4; and

$$N-(CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-R)_3 \qquad (4)$$

G. a variety of di(C-alkyl)-hydroxydiamines and -dihydroxyamines, which are also formed by incomplete amination.

To summarize, a single carbon number 1-epoxyalkane gives about 15 different compounds in various ratios under typical reaction conditions. This ratio of products can be adjusted by changing reaction temperatures, reaction times and ammonia to epoxide ratio.

When two different 1-epoxyalkanes (i.e., epoxides having two different carbon numbers, such as a mixture of C_{18} and C_{20} epoxides) are mixed and reacted with ammonia, the number of compounds produced increases more than just twofold. The dimer and trimer products (B, C, E, F and G above) can now have alkyl groups with more than one carbon number, resulting in products with mixed chain length alkyl groups. These additional products, further increase the number of chemical compounds produced.

A mixtur of three epoxides, such as a mixture of C_{20}, C_{22} and C_{24} epoxides, will give polyalkylenepolyamines which ar a mixture of at least 50 different compounds! It is believed that this polyalkylenepolyamine mixture primarily contains C-alkylethylenediamines (3 compounds) and di-(C-alkyl)-diethylenetriamine (18 compounds) and triamines of Structure 4 (8 compounds).

Surprisingly and unexpectedly, adding a single 1-epoxyalkane having a short chain alkyl group to the starting mixture of LCAG 1-epoxyalkanes has a significant effect on the properties of the produced polyalkylenepolyamine. Indeed, the effect of adding a short chain epoxide is dramatic. It results in a drop in meltpoint of 15 to 20°F, over the polyalkylenepolyamine produced from a mixture of long chain alkyl groups, such as those from C_{20}, C_{22} and C_{24} 1-epoxides. Thus, by adding an effective amount of C_{12}, C_{14}, or C_{16} epoxide starting material, an unbalanced di-(C-alkyl)-diethylenetriamine is produced where one of the two alkyl groups is short and the other is long and thereby gives desirable low melting corrosion inhibitors. The differential scanning calorimetry (DSC) second endpoint is used herein as an equivalent measure of the meltpoint.

Data from polyalkylenepolyamines with different alkyl chain lengths are shown in the following Table. The experimental procedures are detailed herein below.

TABLE 1 - POLYALKYLENEPOLYAMINE DSC ENDPOINTS

Ex. No.	Alkyl chain length[1, 2] No. of Carbons	DSC 2nd Endpoint, °F
3	12	201
4	14	203
5	18,20 22 (52:40:7) mix	205
6	0.5 x_i Ex. 1; 0.5 x_i Ex. 5	181

[1] From epoxide starting materials having two additional carbon atoms.
[2] x_i = mole fraction

As can be seen, polyalkylenepolyamines produced with SCAG, i.e., R = C_{12} (from a C_{14} epoxide starting material) or C_{14} have about the same high melting point (203°F) as polyalkylenepolyamines produced with LCAG, i.e., R = C_{18-22} (from a mixture of C_{20}, C_{22}, and C_{24} epoxide starting materials). Surprisingly and quite unexpectedly, polyalkylenepolyamines produced from a blend of these short chain and long chain epoxide starting materials have a meltpoint that is 5-25°F lower, i.e., less than about 200°F. More preferably the compositions of this invention have meltpoints below 195°F, and most preferably below 190°F.

The presently described reaction of 1-epoxyalkanes and ammonia is normally carried out in a single reactor at a temperature in the range of about 100 to 250°C, preferably in the range of about 150 to 230°C and most preferably in the range of about 160 to 190°C. The thermal reaction, epoxide ring opening occurs at about 120°C. The catalytic reaction, amination, is preferably conducted at about 185°C. The reaction pressure is generally in the range of about 500 to 3,000 psi, and preferably between about 1,500 to 2,500 psi.

The reactor is normally charg d at room temp rature with hydrogen gas to a pressure of about 10 to 400 psi, and preferably to a pressure of about 20 to 50 psi, although hydrogen may not be necessary. The catalyst employed in the reaction may be either supported or unsupported, and is generally present in an amount equal to about 0.1% to 30% of the weight of 1-epoxyalkanes, and preferably 1% to 10% of the weight of 1-epoxyalkanes. A small amount of water is generally added. The reaction will normally proceed over a period of about 1 hour to 20 hours. The resulting polyalkylenepolyamine is isolated simply by flashing the volatile hydrogen, ammonia and water and filtering off the catalyst while hot.

It is also envisioned that the reaction may be carried out in a continuous fashion with similar ratios of ammonia, 1-epoxyalkane and hydrogen passing in a plugflow reactor over a bed of solid catalyst. This continuous process may also allow for separate reaction zones for (1) noncatalytic conversion of the 1-epoxyalkane to alkanolamines mixture, for example in a preheater segment of the continuous reaction unit, and (2) catalytic amination of the alkanolamines mixture to polyalkylenepolyamines.

Amination catalysts for converting alcohols to amines are known in the art and include nickel-containing and cobalt-containing catalysts. Preferred catalysts includ Raney nickel, nickel chromite, supported cobalt catalysts such as Harshaw-Filtrol Co-0138E, supported nickel-rhenium catalysts such as that described in U.S. Patent No. 4,111,840 and supported nickel catalysts such as Harshaw-Filtrol Ni5136P. More preferred catalysts are supported cobalt and supported nickel-rhenium catalysts. Raney nickel is most preferred.

Amine-coated Raney nickel catalyst can be used, for example, tallow amine-coated Raney nickel. This catalyst can be recycled; the recycled catalyst gives substantially identical product.

Minimizing Trialkanolamine Formation

It is believed that one important species contributing to high melt point of these polyalkylenepolyamines are trialkanolamines (TAA) of Structure 4. TAA has a very high melting point and a very low solubility in the solvents used to formulate polyalkenepolyamines into active corrosion inhibitors.

Surprisingly, the production of these undesirable trialkanolamines can be minimized by

1) using a high ammonia to epoxide ratio and
2) controlling the reactor fill factor.

I have discovered conditions that reduce the amount of TAA formed in the reaction. Additionally, I have also discovered an interaction between two process variables that can be exploited to reduce the amount of TAA formed.

An important process variable that controls formation of TAA is the ammonia to epoxide ratio. Increasing the ammonia to epoxide ratio decreases the amount of TAA formed. Preferred ammonia to epoxide ratios are greater than 4 to 1, preferably greater than 6 to 1, and most preferably greater than 9 to 1.

Another important variable that influences TAA formation is referred to herein as "reactor fill factor". The

reactor fill factor is computed using the densities of each liquid or solid reactant at 60°F. Preferred reactor charges vary from 65 to 80% of the total volume of a batch reactor. The pr f rred and maximum reactor fill factors depend on the reactant molar ratio, the rated pressure of the reactant vessel and process economics.

It is preferred that the reaction of the mixture of 1-epoxyalkanes with ammonia takes place in a reactor where 65 to 80% of the reactor volume is liquid, based on calculated liquid volumes at 60°F; preferably about 75% of the reactor volume is liquid. If the reactor fill factor is too high, pressure limits are encountered.

I have also discovered that the useful upper limit to the fill factor is about 80%. At fills greater than this value, the reaction vessel can become hydrostatically loaded during the reaction. This results in an extremely rapid pressure increase from inside the vessel. Unless the vessel can withstand very high pressures, the liquid must be vented through a control or relief system, such as a bursting disc rupture. It is believed that this over-pressurization occurs primarily because of the great expansion factor for ammonia liquid over the temperature range used. However since a considerable amount of ammonia dissolves into the hydrocarbon phase, the exact conditions when the system becomes hydrostatically loaded is difficult to predict.

More importantly, there is a synergistic effect between the ammonia to epoxide mole ratio and the reactor fill factor. The preferred combination of these variables -- high ratio and high fill -- results in a TAA content lower than the sum of the individual effects. For example, raising the ammonia to poxide ratio (from 6:1

to 15.6:1) by itself decreases the TAA content from 9.6 to 8.0 mole percent. Raising the fill factor from 50% to 80% by itself decreases the TAA to 6.2 mole percent. If the effects were additive, one would expect a TAA content of

$$9.6 - [(9.6-8.0) + (9.6-6.2)] = 4.6\%$$

when both the ammonia ratio and the fill factor are raised. Actual data shows TAA contents of about 4.0% when both variables are high. This demonstrates a significant synergistic interaction.

Adjusting the Hydrophobic-Hydrophilic Ratio

Advantageously, the hydrophobic-hydrophilic ratio and nitrogen content of the polyalkylenepolyamine product can be readily adjusted by the addition of various amounts of ethylenediamine or a higher polyethylenepolyamine, such as diethylenetriamine, during the reaction with ammonia. Compounds that produce ethylenediamine (such as ethylenedichloride or higher polyethylene-polyamines can also be used. The amount of ethylenediamine or higher polyethylenepolyamine which may be used will generally range from about 1 to 50 weight percent, and preferably from about 10 to 20 weight percent.

Corrosion Inhibition

The polyalkylenepolyamines of this invention are good corrosion inhibitors. In comparison with commercial corrosion inhibitors, they show much superior performance.

For use as corrosion inhibitors, the polyamines of the invention can be applied to the metal surfaces to be

protected in a variety of ways known to the art. For example, a dilute hydrocarbon solution of the polyamine may be contact d with the metal to be protected, using methods such as dipping, spraying, wiping, and the like. For this method of application, solutions of about 0.1 to 10%, preferably from about 0.2 to 1%, by weight of polyalkylenepolyamine, or mixture of polyalkylene-polyamine and other active corrosion inhibiting agents, are employed.

Alternatively, oil-soluble, water-dispersible formulations of the present polyamines, or mixtures of the polyamines and other active corrosion inhibiting agents, can be added to a corrosive aqueous environment. In this method of application, sufficient amounts of polyamine, or mixture of the polyamine and other active corrosion inhibiting agents, are added to give from about 1 to 1,000 ppm, preferably from 10 to 500 ppm, of active corrosion inhibitor in the final solution for continuous methods of treatment. For batch treatment methods, the level of corrosion inhibiting agents is generally between 500 and 25,000 ppm, preferably between 1,000 and 10,000 ppm.

Corrosion inhibitors are usually formulated with other components for corrosion inhibiting applications. Preferably, the corrosion inhibiting poly-alkylenepolyamine composition of the present invention will be combined with one or more dimer/trimer acids to provide a formulated product. Dimer/trimer acids are organic acids and are well known in the art. They are typically derived from fatty acids. Examples of dimer/trimer acids include Empol 1024, obtained from Emery Chemicals, Union Camp Century D75 and W stvaco DTC 405.

In addition to the polyalkylenepolyamine of the invention and the dimer/trimer acid, corrosion inhibiting formulations may also contain one or more surfactants, one or more alcohols and a hydrocarbon solvent. The surfactant employed may be ionic or nonionic in nature. Generally, nonionic surfactants are preferred. Typical nonionic surfactants include ethoxylated nonylphenols such as Igepal CO-630 and Igepal CO-710, and ethoxylated fatty alcohols such as Tergitol 15-S-9. The hydrocarbon solvent may be any of the known solvents, such as kerosene, diesel fuel, paint thinner, toluene, lubricating oil, and similar materials. A preferred hydrocarbon solvent is a heavy aromatic distillate containing C_9+ aromatics, such as Chevron HAD, sold by Chevron Chemical Company, San Ramon, California. Isopropanol is a typical alcohol.

Generally, the active corrosion inhibiting agents will be combined with a solvent and a surface active agent to produce a concentrated solution of the corrosion inhibitor. In this solution, the polyamine, or mixture of the polyamine and other active corrosion inhibiting agents, will be present in amounts ranging from about 10 to 60%, preferably about 30 to 50%, by weight. The amount of solvent present is from about 30 to 80%, and the amount of surfactant is about 1 to 20%, by weight. This concentrated formulation can then be diluted to the desired concentration of the final solution.

A preferred oil-soluble, water-dispersible formulation will contain about 15 to 30% actives. The term actives as used herein include all components except the hydrocarbon solvent. A typical formulation would include 1-20%, preferably 5-10% of the present p lyalkylenepoly

amine, an approximately equal amount of a dimer/trimer acid, about 1 to 10% of a nonionic surfactant, and about 0 to 5% of an alcohol, such as isopropanol; the remainder is a hydrocarbon solvent, such as Chevron HAD.

Oil-soluble, water-dispersible formulations of the present polyamines are particularly useful in brine/CO_2 or brine/H_2S environments, such as encountered in oil wells, especially oil wells employing secondary oil recovery techniques.

The following examples are provided to illustrate the invention in accordance with the principles of this invention but are not to be construed as limiting the invention in any way except as indicated by the appended claims.

EXAMPLES

Example 1

MEASURING DSC SECOND ENDPOINT OR THE MELTPOINT

The term meltpoint as used herein is the second DSC endpoint. The meltpoint was determined using differential scanning calorimetry (DSC). A Perkin Elmer DSC-2 Model 3500 instrument was used. About 5-10 mg of sample was heated at a rate of 10°C/min. The heat uptake was measured as a function of time. The second DSC endpoint was determined as the maximum temperature at which the heat-up curve returns to the base line.

Figure 2 shows how this value is determined graphically. As can be s en, there are several heat uptakes. A baselin , which is determined by the heating rate, can be readily drawn. The bas line on Figure 2 was computer determined. The maximum temperature at which the actual

heat uptake curve meets this baseline is the second DSC endpoint or meltpoint. This point is labeled "A" on Figure 2.

Example 2
CALCULATION OF REACTOR FILL FACTOR

Fill factor is computed using the charges and densities of the reaction system components and the reactor free internal volume. The densities used are taken at 60°F. For example:

Density of C_{14}/C_{20-24} epoxide = 0.846 g/mL @ 60°F
ammonia = 0.616 g/mL @ 60°F
water = 1.00 g/mL @ 60°F
coated nickel = 1.67 g/mL @ 60°F

The reactor fill factor for a run charging 323.5 gms epoxide, 185.0 gms ammonia, 19.6 gms of water, and 62.0 gms catalyst into a 1000 mL reactor is computed as:

$$\frac{323.5/0.846 + 185./0.616 + 19.6/1.00 + 62/1.67}{1000 \text{ mL reactor volume}} \times 100 =$$

$$= 74\% \text{ reactor fill factor}$$

Example 3
PREPARATION OF C_{14} POLYALKYLENEPOLYAMINE

A C_{14} 1-epoxytetradecane (290.3 g, 1.37 mole) was obtain d from Viking Chemical Company under the trade name "Vikalox 14". It was added to a stirred, 1 liter stainless steel autoclave along with 17.6 g (0.98 mole) of deionized water and 62.0 gms of amine coated Raney nickel catalyst. The catalyst was AMCAT-5 from Activated Metals and Chemicals, Inc. The vessel was pressurized to

25 psig with hydrogen gas. Anhydrous ammonia (232.8 gms, 13.7 mole) was then added. This corresponds to an ammonia to epoxyalkane mole ratio of 10:1. This mixture was heated at 185°C for 3.5 hours. Upon completion of the reaction, the excess ammonia and water were vented and condensed at 130°C. The product was decanted from the catalyst. After cooling, it had a meltpoint of 197°F. Repeat runs at similar conditions gave product with meltpoints of 199 and 207°F. The average meltpoint for the three runs was 201°F.

Example 4

PREPARATION OF C_{16} POLYALKYLENEPOLYAMINE

The procedure of Example 3 was followed, except that Vikalox 16, a C_{16} 1-epoxyalkane was used. The polyalkylenepolyamine product had a meltpoint of 210°F. Additional runs at similar conditions gave products with meltpoints of 201 and 199°F. The average meltpoint for the three runs was 203°F.

Example 5

PREPARATION OF C_{20}-C_{24} POLYALKYLENEPOLYAMINE

A C_{20}-C_{24} 1-epoxy alkane (352 g, 1.12 mole) was obtained from Viking Chemical Company under the trade name "Vikalox 20-24". The starting olefin, prior to epoxidation, was analyzed by gas chromatography and shown to contain 1.2 mole % C_{18} olefins, 51.6 mole % C_{20} olefin, 40.2 mole % C_{22} olefin and 7.0 mole % C_{24} olefin. This mixture was commercially epoxidized. The resulting epoxides were added to a stirred, 1 liter stainless steel autoclave along with 20.2 g (1.12 mole) of deionized water and 60.2 gms of tallow amine coated Raney nickel catalyst (purchased from Activated Metals and Chemicals, Inc.). About 50 weight % of this catalyst is amine. The vessel was pressurized to 20 psig with hydrogen gas.

Anhydrous ammonia (192.9 gms, 11.3 mole) was then added. This corresponds to an ammonia to epoxyalkane mole ratio of 10:1. This mixture was heated at a rate of about 3°/min. until it reached 185°C. This temperature was then maintained for 3.5 hours. Upon completion of the reaction, excess ammonia and water were vented and condensed at 130°C. This product was decanted from the catalyst while hot. After cooling, the product had a meltpoint of 206°F. Several repetitions of this batch preparation under similar reaction conditions produced product with meltpoints of 210, 207, 208, 200, 206, 203, 200 and 205°F. The average meltpoint for these nine runs was 205°F. The preparation was repeated on a large scale under similar mole ratio and reaction conditions. The product had a 207°F DSC endpoint.

Table 1 shows the second DSC endpoints of the products of Examples 3, 4 and 5. As can be seen, polyalkylenepolyamines with long chain alkyl groups (C_{18-22}) and polyalkylenepolyamines with short chain alkyl groups (C_{12} and C_{14}) have about the same meltpoints.

Example 6

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYLENEPOLYAMINES

A C_{20-24} 1-epoxyalkane (1188.7 gms) and 812.3 gms of C_{14} epoxyalkane were melted and then mixed together. This corresponded to a 1:1 molar ratio of the epoxyalkane components. A portion (323.5 gms, 1.24 mole) of the above prepared mixture of 1-epoxyalkanes were added to a 1 liter stainless steel autoclave with 19.6 gms (1.09 mole) of water and 62.0 gms of amine coated Raney nickel catalyst. The reactor was sealed and pressurized to 25 psig with hydrogen. Anhydrous ammonia (185 gms, 10.9 mole) was then add d. The mixture was stirred vigorously and heated to 185°C and held at that temperature for 3.5

hours. At the end of the reaction period, the mixture was cooled and the excess ammonia, hydrogen and water v nted and condensed. The agitation was stopped and excess catalyst allowed to settle. The product was decanted from the dense catalyst layer while hot. After cooling the product had a meltpoint of 178°F. This product is an effective corrosion inhibitor. Additional runs obtained under similar conditions had meltpoints of 181, 181 and 187°F, for an average of 182°F for the four runs.

As can be seen by looking at Table 1, mixing long chain and short chain epoxides produces polyalkylenepolyamines with significantly lower meltpoints, here about 20° lower than either polyalkylenepolyamine alone (i.e., compared to Examples 3 and 5).

Example 7

PREPARATION OF BLENDED C_{14} AND C_{20-24} POLYALKYLENEPOLYAMINE

A C_{14} polyalkylenepolyamine (13.9 gms, 0.0317 mole), prepared as in Example 3 above and having a meltpoint of 197°F, and 61.1 gms (0.0961 mole) of C_{20-24} polyalkylenepolyamine, prepared as in Example 5 above and having a meltpoint of 207°F, were melted separately and then thoroughly blended. The DSC behavior of the blended polyalkylenepolyamines (PAPA's) was determined and is shown in Table 2.

Additional blends were made using different ratios of the polyalkylenepolyamines. The results are summarized in Table 2 below and shown in Figure 1. Figure 1 is a graph of meltpoint vs mole fraction for a blend of C_{20-24} and C_{14} polyalkyl nepolyamines. As can be seen, some reduction in meltpoint of the C_{20-24} polyalkylenepolyamine can be achieved by blending a C_{14} polyalkylenepolyamine. All these blends are effective corrosion inhibitors.

TABLE 2 - POLYALKYLENEPOLYAMINE (PAPA) BLENDS

Blend	C_{14} PAPA grams	C_{20-24} PAPA grams	C_{14} PAPA mole %	C_{20-24} PAPA mole %	DSC endpoint °F
7A	13.9	61.1	25	75	206
7B	30.5	44.5	50	50	198
7C	46.1	28.9	70	30	191

Example 8

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES HIGH AMMONIA, LOW REACTOR FILL FACTOR

A mixture of C_{20-24} 1-epoxyalkane and C_{14} epoxyalkane, 0.5 mole fraction each, were melted and mixed together and corresponded to a 1:1 molar ratio of the epoxyalkane components having a molecular weight of 261. A portion (173.9, 0.67 mole) of the above prepared mixture of 1-epoxyalkanes were added to a 1 liter stainless steel autoclave equipped with external electric based heaters, internal agitator and cooling coils with 6.7 gms (0.37 mole) of water. The reactor was sealed and pressurized to 25 psig with hydrogen. Anhydrous ammonia (177.7 gms, 10.43 mole) was then added (mole ratio of ammonia to epoxide of 15.7). The reactor fill factor was 50%. The mixture was stirred vigorously and heated to 365°F and held at that temperature for 3.5 hours. At the end of the reaction period, the mixture was cooled and the excess ammonia, hydrogen and water vented and condensed. The product was analyzed for TAA content by proton NMR measuring the absorption for the hydrogen atoms alpha to the nitrogen (i.e. those on the number 1 carton atoms) as in Example 11. The product had 5.8 mole % TAA.

Example 9

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES HIGH AMMONIA, HIGH FILL

The procedure of Example 8 was followed except that 278 g of epoxide, 284 g of ammonia (mole ratio 15.7) 10.89 of water were used to give a reactor fill factor of 80%. The product contained 4.1% TAA.

Example 10

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES ADDITIONAL EXPERIMENTS

Additional experiments were performed at various ammonia to epoxide mole ratios and reactor fill factors using the procedure of Example 8 and the amounts of reactants shown in Table 3.

Table 3 shows four pairs of runs, each of which have the same ammonia ratio and fill factor, and differ (within the pair) by the water ratio. The water ratio was determined to have no effect on the TAA content. Thus, the TAA content for each pair can be averaged to show the interaction effect.

TABLE 3

Alkanolamine Runs Using C_{14}/C_{20-24} Blended Epoxides

Design order	Feeds, grams charged			H2, psig	Mole ratio		Fill[1] factor	TAV[2]	TAA[3]
	Epoxide	NH3	Water		NH3	H2O			
1	173.9	177.7	6.72	25	15.7	0.56	0.50	149	5.8
2	424.1	154.7	49.15	25	5.6	1.68	0.80	141	8.5
3	265.1	96.7	30.7	25	5.6	1.68	0.50	132	9.7
4	271.0	276.8	31.4	25	15.7	1.68	0.80	160	3.8
5	442.2	161.3	17.1	25	5.6	0.56	0.80	138	7.6
6	278.0	284.0	10.75	25	15.7	0.56	0.80	154	4.1
7	276.0	100.8	10.8	25	5.6	0.57	0.50	127	9.4
8	169.4	173.0	19.6	25	15.7	1.68	0.50	141	6.7

[1] Fill Factor %/100%

[2] TAV = Total Amine Value

[3] TAA = Trialkanolamine

The data from Table 3 is simplified in Table 4 below.

TABLE 4

Pair	Ratio[1]	Fill[2]	Avg. TAA, %
4 & 6	High	High	4.0
2 & 5	Low	High	6.2
1 & 8	High	Low	8.0
3 & 7	Low	Low	9.6

[1] Ammonia to epoxide ratio
[2] Reactor fill factor

As can be seen, high ammonia to epoxide ratios and high reactor fill factors give reduced amounts of TAA. Since TAA has a high meltpoint, low solubility, and does not further aminate to give polyalkylenepolyamines, it is desirable to minimize its production.

The mixture of products produced in Examples 8, 9 and 10 can be further aminated with ammonia and Raney nickel to give polyalkylenepolyamines of this invention. The polyalkylenepolyamines produced at high mole ratios and high fill factors will have lower meltpoints.

Example 11
TRIALKANOLAMINE CONTENT BY NMR

Proton NMR spectra were used to quantitate alkanolamine conversion, selectivity to polyalkylenepolyamines and trialkanolamine (TAA) formation.

A General Electric QE-300 Plus NMR spectrometer with a 5mm dual (^{13}C and ^{1}H) probe was used. The samples were dissolved and heated to 50°C in chloroform to keep the TAA in solution.

The most prominent features in the spectrum are:

1) The large methylene envelope between 1.0-1.5 ppm,
2) The methyl triplets at about 0.75 ppm, and
3) The functional groups of interest (<u>H</u>-C-NRR' and <u>H</u>-C-OH) located between 2.0-4.0 ppm.

The major spectral features are due to methyl and methylene absorbances since those groups comprise the majority of the molecule.

Figure 3 is an expansion of an NMR spectrum showing the amine/alcohol absorbance region of interest (2.0-4.0 ppm). There are three sets of doublets of doublets (4 peaks in each set) between 2.7 and 3.0 ppm which can be used to calculate both the conversion and selectivity. Each of these doublets of doublets corresponds to a single proton in the molecule. The heights of these peaks are used to calculate both the residual reactive alkanolamine and the piperazine content.

The first set is found between 2.7-2.8 ppm. It is associated with the desired amine product. The second set (2.8-2.9 ppm) is associated with reactive primary and secondary alkanolamines. The third set (2.9-3.0 ppm) is associated with piperazine by-products.

Two clusters of peaks between 3.4-3.8 ppm correspond to the protons attached to hydroxyl carbons (<u>H</u>-C-OH). The broad peak between 3.4-3.55 is assigned to the primary and secondary alkanolamines (AA). The broad peak between 3.55-3.8 ppm is due to the trialkanolamine (TAA) <u>H</u>-C-OH protons.

The mole percent TAA is calculated by the following formula:

$$\text{Mole \%} = 100 \times \frac{\text{integrated area of TAA peaks}}{\text{integrated area between 2.0-4.0 ppm}}$$

TAA content is calculated from the spectrum integration over the expanded range of 2.0-4.0 ppm.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention described therein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A corrosion-inhibiting polyalkylenepolyamine composition comprising: a di(C-alkyl)-diethylenetriamine of the general structure

$$H_2N-CHR^1-CHR^2-\underset{\underset{H}{|}}{N}-CHR^3-CHR^4-NH_2$$

where either R^1 or R^2 is hydrogen and either R^3 or R^4 is hydrogen, and where the remaining two non-hydrogen R groups are independently either:

(i) a long chain alkyl group having between 18 to 22 carbon atoms; or

(ii) a short chain alkyl group having between 8 to 16 carbon atoms;

provided that, if both alkyl groups on the di(C-alkyl)-diethylenetriamine are long chain, (i), or both alkyl groups are short chain, (ii), then the composition contains a mixture of di(C-alkyl)diethylenetriamines, some of which have long chain alkyl groups and some of which have short chain alkyl groups.

2. The polyalkylenepolyamine composition according to claim 1 wherein said di(C-alkyl)-diethylenetriamine is unbalanced, having one long chain alkyl group from (i) and one short chain alkyl group from (ii).

3. The polyalkylenepolyamine composition according to claim 1 where the short chain alkyl group has 8 to 14 carbon atoms.

4. The polyalkylenepolyamine composition according to claim 3 where the short chain alkyl group has 10 to 12 carbon atoms.

5. The polyalkylenepolyamine composition according to claim 1 where said di(C-alkyl)-diethylenetriamine comprising between 5 and 60 mole percent of the total composition.

6. The polyalkylenepolyamine composition according to claim 5 where the mole percent of said di(C-alkyl)-diethylenetriamine comprises between 5 and 45 mole percent of the total composition.

7. The polyalkylenepolyamine composition according to claim 6 where the mole percent of said di(C-alkyl)-diethylenetriamine comprises between 10 and 40 mole percent of the total composition.

8. The polyalkylenepolyamine composition according to claim 2 where the mole percent of said unbalanced di(C-alkyl)-diethylenetriamine comprises between 2.5 and 30 mole percent of the total composition.

9. The polyalkylenepolyamine composition according to claim 8 where the mole percent of said unbalanced di(C-alkyl)-diethylenetriamine comprises between 5 and 20 mole percent of the total composition.

10. The polyalkylenepolyamine composition according to claim 2 having a meltpoint below 195°F.

11. A polyalkylenepolyamin composition comprising a mixture of structur s which includes:

(a) at least two C-alkylethylenediamines and

(b) at least two di(C-alkyl)-diethylenetriames or di(C-alkyl)-piperazines, or a mixture thereof; wherein the alkyl groups on (b) are unbalanced containing both (i) long chain alkyl groups of between 18 and 22 carbon atoms and (ii) short chain alkyl groups of between 8 and 16 carbon atoms.

12. The polyalkylenepolyamine composition according to claim 11 where the short chain alkyl group has 12 to 14 carbon atoms.

13. The polyalkylenepolyamine composition according to claim 11 where the short chain alkyl groups comprise at least 10 percent of the total number of C-alkyl groups.

14. The polyalkylenepolyamine composition according to claim 11 where the ratio of (i) to (ii) is in the range of 0.2:1 to 3:1.

15. A method of making the polyalkylenepolyamine composition of claim 2 which comprises:

a) preparing a mixture of functionalized alpha-olefins having between 10 to 24 carbon atoms and having both long chain alkyl groups (i) and short chain alkyl groups (ii); and

b) reacting said functionalized alpha-olefin mixture with ammonia and optionally an amination catalyst to form a polyalkylenep lyamine composition comprising an unbalanced di(C-alkyl)-diethylenetriamine structure.

16. The method of claim 15 wherein said functionalized alpha-olefin mixture is a mixtur of alpha-olefin epoxides.

17. The method of claim 16 wherein the long chain alkyl group of said epoxide is a mixture having between 18-22 carbon atoms.

18. The method of claim 17 wherein the short chain alkyl group of said epoxide has between 10 to 16 carbon atoms.

19. The method of claim 18 wherein the short chain alkyl group of said epoxide has between 12 to 14 carbon atoms.

20. A method of inhibiting corrosion of a corrodible metal material comprising contacting a metal material with an effective amount of the polyalkylenepolyamine composition of claim 1.

21. The method of claim 20 wherein said polyalkylenepolyamine composition comprises a di(C-alkyl)-diethylenetriamine which is unbalanced, having one long chain alkyl group and one short chain alkyl group.

22. A method of inhibiting corrosion in an oil well of a corrodible metal material comprising contacting a metal material with an effective amount of the polyalkylenepolyamine composition of claim 1.

23. The method of claim 22 wherein said polyalkylenepolyamin composition comprises a di(C-alkyl)-diethylenetriamine which is unbalanced, having one long chain alkyl group and one short chain alkyl group.

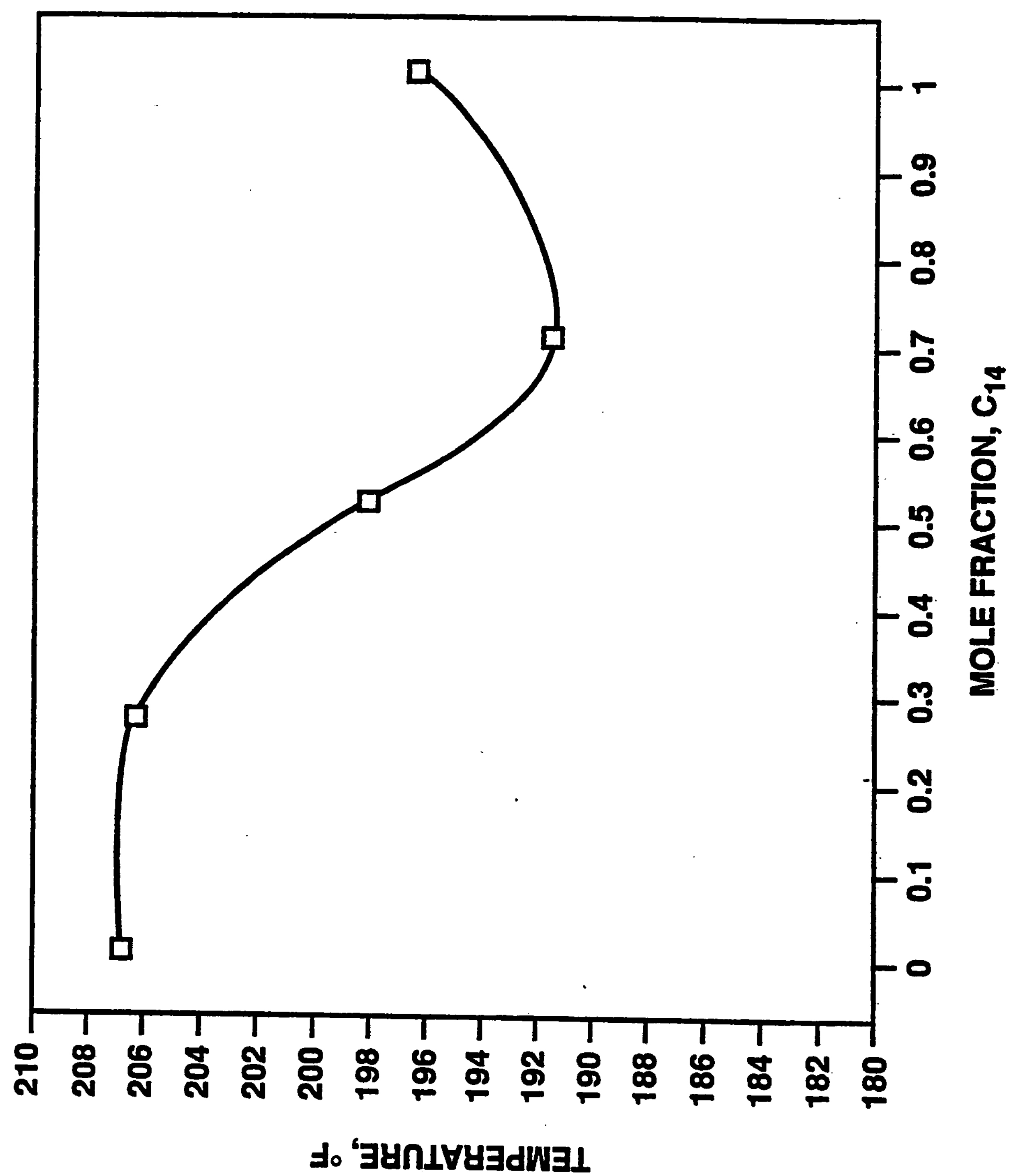
24. A method of minimizing trialkanolamine formation in polyalkylenepolyamine compositions comprising, reacting an alpha-olefin epoxide or a mixture of alpha-olefin epoxides, having at least 10 carbon atoms, with ammonia in a reactor wherein 65 to 80% of the reactor volume is liquid, based on calculated liquid volumes at 60°F.

25. The method of claim 24 wherein about 75% of the reactor volume is liquid.

26. The method of claim 24 where the ratio of ammonia to epoxide is greater than about 6 to 1.

27. The method of claim 26 where the ratio of ammonia to epoxide is greater than about 9 to 1.

FIGURE 1


TEMPERATURE, °F
210
208
206
204
202
200
198
196
194
192
190
188
186
184
182
180
MOLE FRACTION, C_{14}
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0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

FIGURE 2

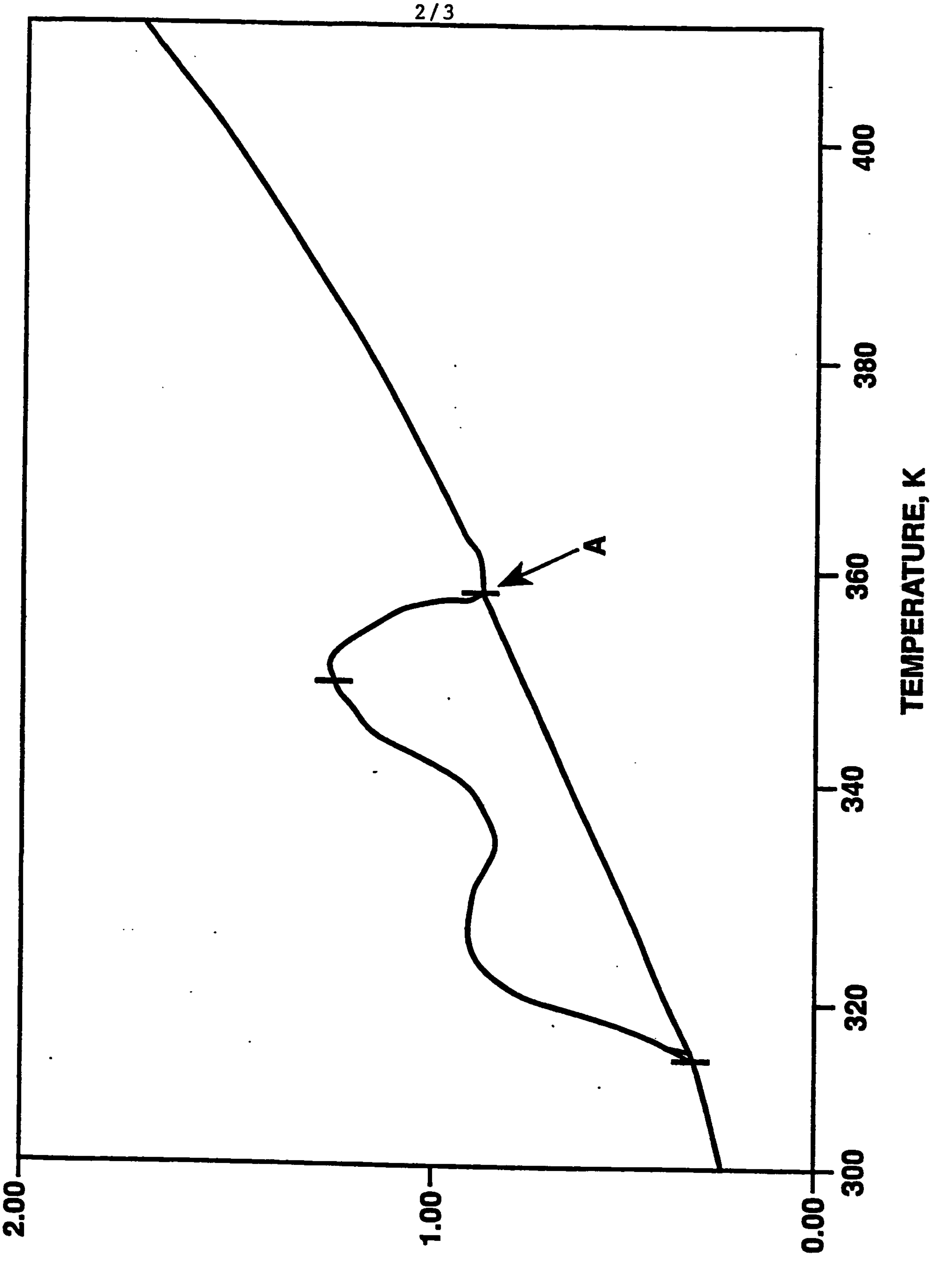
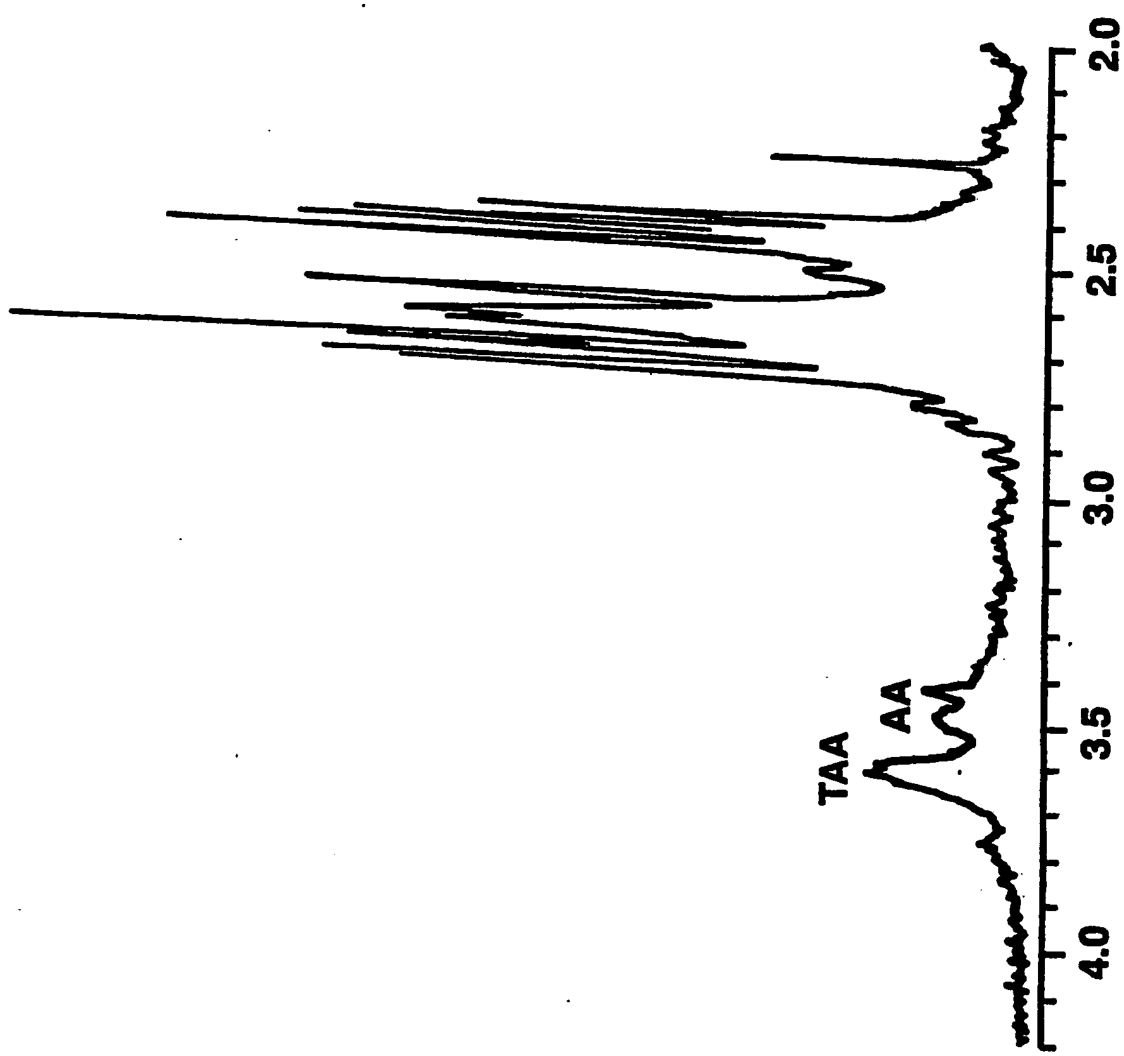


FIGURE 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/01392

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) :C23F 11/14
US CL :252/390,8.555;422/16
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/390,8.555;422/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,900,458 (Schroeder et.) 13 February 1990, see column 41, lines 25-38, col. 5 lines 59-63 and col. 9 lines 65-69.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
18 MAY 1993	09 JUN 1993

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	VALERIE FEE